Example 1

1. *Calculate the bond length of CO from a rotational band line spacing of 3.86 cm*$^{-1}$.

The rotational constant is easily obtained from the rotational line spacing for a rigid rotator

$$\nu = 2B(J+1) \quad \longrightarrow \quad \Delta\nu = 2B \quad B = 1.93\ \mathrm{cm}^{-1}$$

The rotational constant is related to the moment of inertia I by

$$B = \frac{h}{8\pi^2 c I}$$

The moment of inertia around the symmetry axis is

$$I = m_r r^2 \qquad m_r = \frac{m_C m_O}{m_C + m_O}$$

where r is the bond length (distance between C and O) and m_r is the reduced mass,

$$m_r = \frac{12(16)}{12+16} 1.66 \times 10^{-27}\ \mathrm{kg} \ = 1.14 \times 10^{-26}\ \mathrm{kg}$$

Therefore the bond length is

$$r^2 = \frac{h}{8\pi^2 c B m_r}$$

$$r^2 = \frac{6.626 \times 10^{-34}\ \mathrm{J\ s}}{79.0(3.00 \times 10^8\ \mathrm{m/s})(193\ \mathrm{m}^{-1})(1.14 \times 10^{-26}\ \mathrm{kg})} = 1.27{\times}10^{-20}\ \mathrm{m}^2$$

$$r = 1.13\mathrm{A}$$

Example 2

1. *According to the HITRAN database the ozone line at 1020.3189 cm*$^{-1}$ *has an air broadened halfwidth of .0706 cm*$^{-1}$ *at 1 atm* ($p_0 = 1013.25$ *mb) and* $T_0 = 296$ *K and a temperature coefficient of* $n = .76$*.*

a) What is the Lorentz halfwidth at 20 km where the pressure is 53.7 mb and the temperature is 215 K?

Self broadening can be ignored for ozone, so the pressure dependence is obtained from

$$\alpha = \alpha_0 \left(\frac{p}{p_0}\right)\left(\frac{T_0}{T}\right)^n$$

$$\alpha = (.0706\ \mathrm{cm}^{-1})\left(\frac{53.7\ \mathrm{mb}}{1013.25\ \mathrm{mb}}\right)\left(\frac{296\ \mathrm{K}}{215\ \mathrm{K}}\right)^{0.76}$$

$$\alpha = (.0706\ \mathrm{cm}^{-1})(0.0530)(1.275)\ = 0.0048\ \mathrm{cm}^{-1}$$

b) What is the Doppler halfwidth at half max?

The Doppler width is

$$\alpha_D = \nu_0 \sqrt{\frac{2k_B T}{mc^2}} = \sqrt{\frac{2(1.38 \times 10^{-23}\ \mathrm{J/K})(215\ \mathrm{K})(6.02 \times 10^{26}\ \mathrm{kmol^{-1}})}{(48\,\mathrm{kg/kmol})(3 \times 10^8\ \mathrm{m/s})^2}}$$

$$\alpha_D = (1020.3189\,\mathrm{cm^{-1}})(9.09 \times 10^{-7}) \ = 0.00093\,\mathrm{cm^{-1}}$$

The halfwidth is $\alpha_D\sqrt{\ln 2} = 0.00077\,\mathrm{cm^{-1}}$, which is about six times smaller than the pressure broadened width at this altitude.